

Direct observation of surface diffusion of large organic molecules at metal surfaces: PVBA on Pd(110)

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The bonding and surface diffusion of 4-trans-2-(pyrid-4-yl-vinyl) benzoic acid (PVBA) on Pd(110) was investigated by variable temperature scanning tunneling microscopy at sample temperatures between 300 and 450 K. PVBA is a large organic molecule designed for nonlinear optics applications. At low coverages single PVBA molecules are randomly distributed at the surface where they bind diagonally to three neighboring Pd-rows, leading to four equivalent adsorption configurations. The “dog-bone” molecular structure could be resolved. The molecules’ surface diffusion is strictly one-dimensional along the close-packed $[1\bar{1}0]$ -direction of the surface Pd atomic rows and obeys an Arrhenius law with an activation barrier of 0.83 ± 0.03 eV and an attempt frequency of $10^{10.3 \pm 0.4}$ s⁻¹. © 1999 American Institute of Physics. [S0021-9606(99)71010-X]

Scanning tunneling microscopy (STM) provides unique information on adsorbed molecular species and molecular phenomena at surfaces.¹ While simple molecules were employed in initial observations, recent research revealed the potential of STM for studying epitaxial growth of organic thin films on conducting substrates.^{2,3} Large organic molecules are *the* basic elements in the field of molecular electronics and their adsorption behavior is thus of high current interest.⁴ So far predominantly static aspects or direct manipulation of such molecules have been addressed.⁵ However, to fully understand their ordering and interactions at metal substrates, a necessary prerequisite for further developments in the field, an understanding of their surface kinetics is indispensable.

In the present paper we report the first direct study of the surface diffusion of a large organic molecule chemisorbed on a metal surface. In contrast to thermal motions of adsorbed atoms or simple molecules, which frequently can be rationalized straightforward in a single particle hopping model, due to the more complex binding geometry including the possibility of conformational changes and both rotational and internal degrees of freedom, a rather complex scenario of the surface diffusion of large molecules might be expected.⁶⁻⁹ However, to date there is a lack of systematic direct investigations, even if macroscopic techniques such as laser-induced thermal desorption (LITD) were employed to address this problem.¹⁰ As a model system to study surface diffusion of large molecules under well defined conditions, we have chosen PVBA (4-trans-2-(pyrid-4-yl-vinyl) benzoic acid) adsorbed on a Pd(110) single crystal surface. PVBA is an asymmetric organic molecule with a mass of 225 amu. It was designed for nonlinear optics applications.¹¹ As a substrate we have chosen an fcc(110) surface, where due to the substrate anisotropy, one-dimensional surface diffusion or one-dimensional molecular ordering could be expected. The

data demonstrate the successful application of temperature controlled STM for a direct analysis of the large molecules’ thermal motion.

The experiments were performed with a home-built variable temperature STM operational in the temperature range 40–800 K, incorporated in a standard ultrahigh vacuum (UHV) chamber, similar to equipment described elsewhere.¹² The Pd(110) crystal was prepared by cycles of argon ion sputtering (700 eV, $4 \mu\text{A}/\text{cm}^2$) and subsequent annealing (1000 K) resulting in large defect free terraces of typically 1000 Å width. Due to the PVBA molecules’ high stability and low vapor pressure, a molecular beam can be generated by thermal evaporation under UHV conditions.¹³ PVBA was thus deposited by a conventional Knudsen-cell at background pressures of $\approx 2 \times 10^{-10}$ mbar. The employed deposition rate was $\approx 3 \times 10^{-5}$ ML/s as calibrated by STM data [1 monolayer (ML) corresponds to one adsorbed molecule per Pd surface atom]. The STM measurements were performed in the constant current mode with typical tunneling voltages of ± 1 V and currents below 1 nA, i.e., in the high tunneling resistance regime (> 1 GΩ). It was impossible to manipulate the adsorbed molecules under any tunneling conditions, which reflects a strong substrate–adsorbate interaction. We also investigated the possibility of tip-induced changes in the surface diffusivity, however, no modifications in the diffusion characteristics were observed at the employed high tunneling resistances.

A high resolution STM image with a small amount of PVBA evaporated on the Pd(110) surface is depicted in Fig. 1(a). The image reveals the ordering and adsorption geometry of PVBA molecules. The individual molecules lie flat on the surface and are imaged as 1.25 Å high protrusions with a length of ≈ 11 Å. The STM shape is in accordance with the geometrical distance between the extremal atoms of an isolated molecule [12.3 Å in the unrelaxed configuration (Ref. 11)], the chemical structure formula of which is represented in the inset in Fig. 1(a). The molecule consists of a pyridyl

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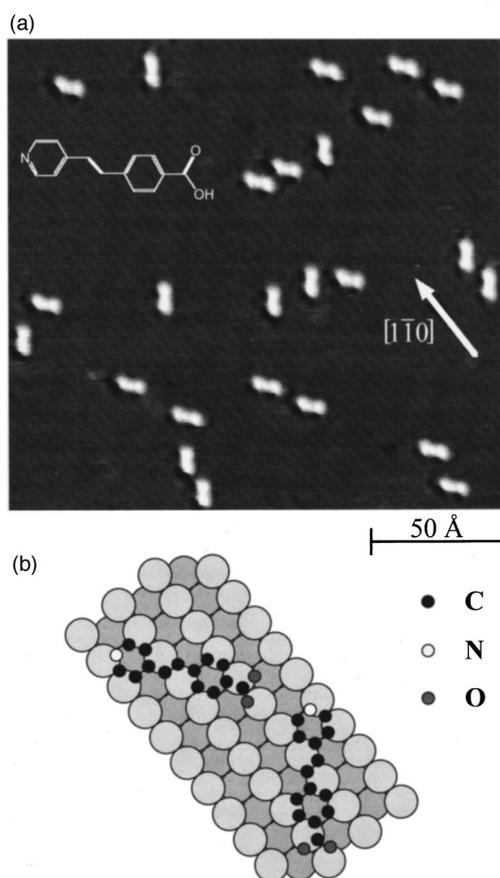


FIG. 1. (a) PVBA molecules randomly distributed on the Pd(110) surface at low coverage ($\Theta = 0.018$ ML). The molecules were adsorbed and imaged at a substrate temperature of 325 K and deposited with a rate of 3×10^{-5} ML/s. The atomic rows of the Pd substrate and the “dog-bone” internal molecular structure are resolved (image size: $190 \times 180 \text{ \AA}^2$; $U_t = 1.04$ V, $I_t = 1$ nA). The chemical structure formula of 4-trans-2-(pyrid-4-yl-vinyl)benzoic acid (PVBA) is depicted in the inset. (b) Ball model for unrelaxed PVBA molecules on Pd(110). Light (dark) grey circles: Pd atomic rows of the surface (second) layer; small circles: individual PVBA atoms (omitting H atoms). The molecular axis is oriented by $\pm 35.3^\circ$ with respect to the $[1\bar{1}0]$ Pd rows providing optimal coordination of surface Pd and molecular subunits.

group attached to a benzoic acid via a vinyl group. The corresponding “dog-bone” internal molecular structure, which is associated with the two coupled molecular carbon-ring systems, is clearly discernable. The molecules are randomly distributed at the surface, which also holds for adsorption conditions with high molecular mobility or upon annealing of the surface. This indicates that molecule–substrate interactions by far exceed the intermolecular interactions. The molecular axis is oriented by $\pm 35^\circ$ with respect to the close-packed $[110]$ surface directions. A detailed analysis of the STM data reveals a binding of the molecules to three neighboring Pd atomic rows, as demonstrated by the ball model in Fig. 1(b) (whereas the position in $[001]$ is certain, the position of the molecule in $[1\bar{1}0]$ could not be exactly determined as atomic resolution of the substrate in this direction could not be achieved in the presence of the molecules). The data are in agreement with STM observations on the systems benzene/Pd(110)¹⁴ and benzene/Ni(110)¹⁵ where the C-ring

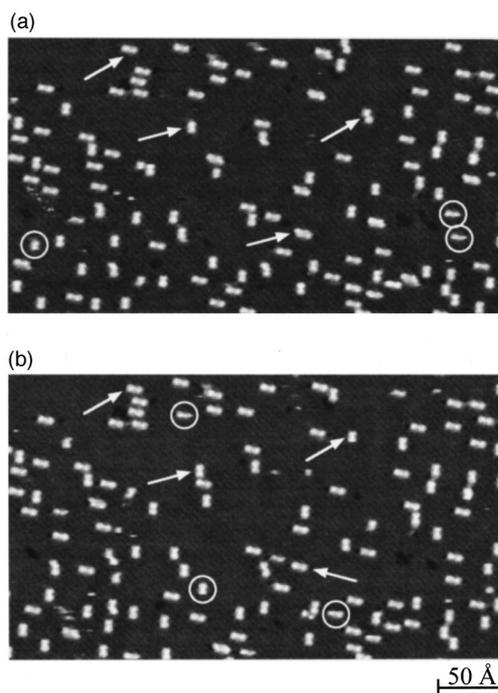


FIG. 2. Series of STM images monitoring thermal motions of PVBA molecules on Pd(110) at $T = 361$ K (image sizes: $360 \times 200 \text{ \AA}^2$; $U_t = 1.20$ V, $I_t = 0.4$ nA). The time lapse between the two consecutive images is 220 s. Arrows indicate molecules whose position changed revealing the one-dimensional nature of the surface diffusion; circles mark molecules moving under the STM tip which are fractionally imaged.

was found at the fourfold hollow site of the substrate. The two different ends of the molecule did not exhibit different STM imaging characteristics. This is ascribed to a transparency of the carboxylic groups in the STM imaging process, which was similarly reported for adsorbed fatty acids.¹⁶ The adsorption geometry reflects optimal coordination of the molecular subunits and the palladium surface atoms achievable without strong distortions of neither intramolecular nor substrate structure. The results indicate that the surface chemical bond of the organic molecules with the Pd substrate is predominantly due to π -binding via the electron ring systems of the pyridyl and the benzyl group, respectively.^{17,18} Due to the substrate symmetry and molecular asymmetry four equivalent molecular configurations are possible. Since the molecular end groups are not differentiated, only the two different orientations with respect to the $[110]$ Pd atomic rows can be discriminated.

A molecule aligned in one orientational configuration cannot be transformed into the mirror configuration by a simple rotation for symmetry reasons. Rather, the molecule would have to be flipped about its own axis in addition. This is believed to be a reason why molecular rotations were not directly observed. In contrast, the thermal motion of individual molecules could be monitored. A series of STM images demonstrating molecular surface diffusion at a substrate temperature of 361 K is reproduced in Fig. 2. The data were recorded at the same area with a time lapse of 220 s between the two images shown. Two effects due to the thermal mobility can be discerned upon inspection of the data. On the

one hand, a comparison of consecutive images reveals that a fraction of the molecules changed position in the time interval between the recording. An analysis of the positional changes demonstrates that the PVBA surface diffusion is strictly one-dimensional along the close-packed substrate direction. The molecular displacements are thus exclusively along $[\bar{1}10]$. This holds similarly for higher temperatures and reflects the anisotropy of the fcc(110) surface which results in different diffusivities along the primitive surface directions, earlier observed for simpler molecular adsorption systems.^{19,20} On the other hand, the imaging characteristics of single molecules within an individual STM image are subject to surface diffusion: since the imaging of the molecule requires a certain number of line scans and thus a certain time interval, there is a probability that molecules diffuse away from the area under the STM tip while recording the images. Thus the limited residence time at a specific site leads to an incomplete imaging of a fraction of the molecules. They show up in a reduced number of neighboring scanlines before they hop away during the measurement, whereupon characteristic ‘‘cut-off’’ features in the topographs are created (marked by circles in Fig. 2). These features are used to analyze the molecular surface diffusion with the present system.

The hopping rates are obtained from the number of scanlines where molecules are imaged at their original sites: the probability that a particle remains at a given site after time τ is $P(\tau) = \exp(-\nu_s\tau)$, where ν_s is the hopping rate to be determined. τ is chosen such that it corresponds to the time necessary to image a molecule entirely, for which the number of scan lines times the scanning period (of the fast x -direction) was taken. Accordingly, $(1 - P(\tau))$ is the fraction of molecules which jumped within this time interval and the rates can be obtained from a statistical analysis of series of images. With the present system, the two orientational configurations of the molecule provide an additional check of this method. Since the fast scan direction is not parallel to the Pd surface atomic rows, the number of line scans for complete imaging of molecules in the respective configurations differ. However, the analysis of the individual geometries agree well and the same hopping rates are obtained. The temperature range accessible with the present system and instrumentation is the region 330–370 K. In addition, experiments employing different scan rates were performed, which substantiate the above statement that the molecular surface diffusion is unaffected by the STM tip.

The statistical hopping frequency analysis is plotted in the Arrhenius representation in Fig. 3. The results clearly demonstrate that the one-dimensional motion of the large organic molecule obeys an Arrhenius law. The linear fit of the data yields an activation barrier of 0.83 ± 0.03 eV. The corresponding attempt frequency amounts to $\nu_0 \approx 10^{10.3 \pm 0.4} \text{ s}^{-1}$. The fact that the molecules' migration can be described by an Arrhenius law indicates that a single process is decisive for the motion of the molecules and that possible complexities due to the large molecular size do not result in extraordinary diffusion characteristics. Although the corrugation potential experienced by the large molecule is believed to be much more complex than that of an adsorbed

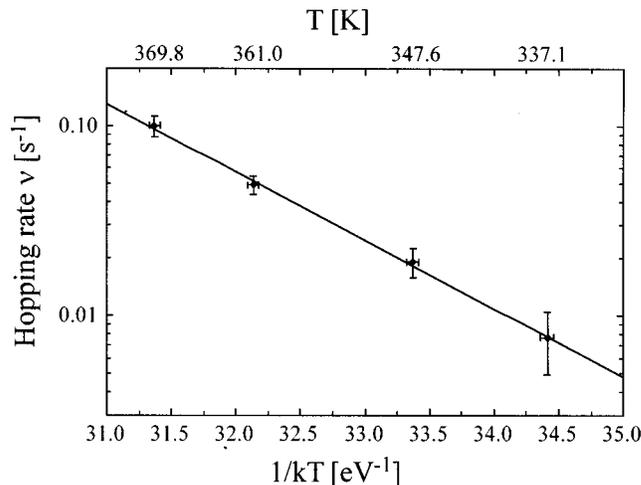


FIG. 3. Arrhenius plot of single molecule hopping rates along the $[\bar{1}10]$ substrate direction in the temperature interval between 335 and 370 K. The surface diffusion of the large organic molecule obeys an Arrhenius law with an energy barrier of 0.83 ± 0.03 eV and an attempt frequency of $10^{10.3 \pm 0.4} \text{ s}^{-1}$.

simple molecule or atom, and intramolecular degrees of freedom might interfere, the molecular surface diffusion can be described in simple terms. In agreement, molecular dynamics simulations of surface diffusion of n -alkanes report that an Arrhenius expression adequately describes large molecular motions for which complex diffusion mechanisms exist.^{6,8} The migration barrier of the adsorbed molecules *per se*, is high and signals a rather strong bonding of the molecules to the Pd surface. Whereas for small adsorbates migration barriers (E_m) are typically $\approx 10\% - 20\%$ of the binding energy (E_b), higher ratios of $\approx 30\%$ have been reported for larger molecules,¹⁰ which would imply $E_b \approx 2.8$ eV with the present system. This compares well with the significantly higher mobility of benzene adsorbed at the same surface,¹⁴ where a weaker surface chemical bond is formed ($E_b \approx 1$ eV).²¹ Similar $E_m - E_b$ trends were reported for surface diffusion of n -alkanes on Ru(001),¹⁰ studied by LITD experiments. With these investigations it was also observed that the diffusion coefficients (D_0) associated with the large molecules' surface diffusion are much larger than would be expected from a hopping model where the molecules jump just by one surface lattice constant. Long jumps were suggested as a possible explanation for this behavior,^{8,10} however it must be noted that the LITD results have been obtained by means of an integral, nonlocal technique, where the ubiquitous surface defects such as atomic steps may interfere. Our data are in agreement with statistics expected from one-dimensional next-neighbor hopping and exclude the possibility of the rather long jump lengths (40–50 Å) invoked for the interpretation of n -alkanes' surface diffusion on Ru(001) LITD results,¹⁰ where we are dealing however, with weakly bound molecular species. Nevertheless, a precise quantitative analysis of the jump length is not possible with the present investigation due to slight thermal drift distortion obscuring comparison of consecutive images, so that a small fraction of molecular jumps over two or three lattice sites cannot be entirely ruled out. Assuming single site molecular hopping,

an intrinsic diffusion coefficient of $D_0 = \frac{1}{2}a^2\nu_0 = 7.55 \times 10^{-6} \text{ cm}^2/\text{s}$ for the one-dimensional motion is obtained. The results ascertain that the attempt frequency associated with the molecular motion is about two orders of magnitude smaller than that of benzene on Pd(110), where estimates signal $\nu_0 \approx 10^{12} \text{ s}^{-1}$.^{14,22} The small attempt frequency with the present system possibly indicates a bonding configuration with reduced entropy in the transition state leading to an effective attempt frequency reduction. Further theoretical investigations are suggested to clarify this issue.

In conclusion, we demonstrated that variable temperature STM is a well performing tool to investigate surface diffusion of adsorbed large organic molecules with high precision. It is suggested that this technique will be of general use in studies concerning the kinetics of adsorbed large molecular species at surfaces.

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